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**CATALYSIS BY ATOMIC-SIZED CENTERS: METHANE ACTIVATION FOR PARTIAL OXIDATION AND COMBUSTION**

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<b>14. ABSTRACT</b> <p>The overall goal of this work has been to find chemical and modifications of oxide surfaces that boost their catalytic performance for alkane conversion. Experimental work is done in collaboration with UCSB Professors Michael J. Gordon and Eric W. McFarland. We have examined a large number of modifications: doping with higher-valence or lower-valence cations, halogenating the surface, delaminating some oxides to turn them in two-dimensional materials, creating submonolayers of oxides supported on other oxides or on metals, or promoting oxide catalytic chemistry by using molten salts. Based on calculations on a variety of oxide-molecule systems, we proposed a set of general rules that give guidance regarding which surface modifications will improve alkane activation by an oxide catalyst and reduce the number of calculations that need to be performed when analyzing a specific oxide catalyst for a specific alkane. For example, the presence of an acid on a surface will change the site to which a base will bind and will increase substantially the binding energy of the base. This strong acid-base interaction takes place through the oxide; the base does not bind to the acid. The acid will influence the binding of the base even if the binding site is several lattice sites away. The same phenomena occur if an acid binds to a surface on which a base is present. Prior to this work it was assumed that in the presence of another species, a molecule will bind to the site to which it binds when it is alone on the surface; this is not true if one molecule is an acid and the other is a base. These rules have been used to guide us in deciding which modifications of an oxide surface will increase the catalytic activity for alkane activation. Essentially we found that all lower-valence dopants will activate surface oxygen, making the Mars-van Krevelen mechanism for alkane partial oxidation more efficient. Higher-valence dopants will adsorb O<sub>2</sub>, transfer electrons to it, and make it mo</p>			
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## Modified Oxides”

The recent availability of alkanes (C1-C4) from cheap natural gas has created great industrial and scientific interest in catalysts that convert alkanes into valuable chemicals. There is abundant literature showing that oxides catalyze extremely interesting and useful alkane reactions but in almost all cases the performance is not good enough for commercial utilization. The goal of our research is to use experiments and theory to find chemical and morphological modifications of oxide surfaces that will boost their catalytic performance for alkane conversion. This AFOSR grant supports the theoretical work but the two aspects of our research are intimately linked and there is no clear demarcation between them. We have examined a large number of modifications: doping with higher-valence or lower-valence cations, halogenating the surface, delaminating some oxides to turn them in two-dimensional materials, creating submonolayers of oxides supported on other oxides or on metals, or promoting oxide catalytic chemistry by using molten salts.

With support from this grant, we have published twenty-two papers [1-22], submitted two manuscripts[23-24], and have written two manuscripts that will be submitted soon to the *Journal of Physical Chemistry* [25-26]. One Ph.D. dissertation was produced (see Appendix). While our main focus is catalysis by oxides we have explored other related areas as outlined below.

Besides the PI, Horia Metiu, the following people have been involved in the research effort (in alphabetical order): Vishal Agarwal (postdoc), Abhinav Anand (undergraduate student), Steeve Chrétien (postdoc), Zhenpeng Hu (postdoc), Chang Huang (visiting graduate student), Henrik H. Kristoffersen (postdoc), Bo Li (postdoc), XiaoYing Sun (visiting postdoc), Suheng Wang (visiting undergraduate student), Jie Yu (graduate student).

Because of the variety of the work presented here we organize the report into several sections.

**(1) A general set of qualitative rules.** Our work on catalysis by oxides has been guided by a paradigm first noted by us in 2007 and fully developed in subsequent work[1-7,10-11,22]. Two review articles[5-6] present a synthesis of our conclusions. Based on a large number of calculations on a variety of oxide-molecule systems we proposed a set of general rules. (1) There is a very strong interaction between Lewis bases (electron donors) and Lewis acids (electrons acceptors) when they are coadsorbed on an oxide surface. Lewis acids important for alkane activation by oxides are oxygen, halogens, and oxide surfaces doped with a lower-valence dopant. Important Lewis bases for alkane activation are H adsorbed on surface, alkyls adsorbed on the surface, and oxygen vacancies in the oxide. Obviously the chemistry of alkane on oxide surfaces, which consists mainly of partial oxidation reactions, involves both acids and bases and this is why these rules are important. (2) If two amphoteric molecules or molecular fragments (formed by dissociative adsorption) are present on a surface, one will adsorb on a surface site that allows it to be a Lewis acid and the other on a site that allows it to be a Lewis base. For example, H adsorbed alone on an oxide surface will bind to oxygen to form a hydroxide. However, if a Lewis base (e.g. any electron donor) is already present on the surface, hydrogen will adsorb on a cation to make a hydride (negatively charged H). The essential observation is that the presence of an acid on a surface will change the site to which a base will bind, and vice-versa. Prior to this work it was assumed that in the presence of another species a molecule will bind to the site to which it binds when it is alone on the surface; this is not true if one molecule is

an acid and the other is a base. (3) This acid-base interaction is “through oxide” and it is not because the acid reacts (forms a chemical bond) with the base. (4) The interaction is long-ranged, meaning that it does take place even if the acid and the base are separated by several lattice sites or if the acid is buried in the third layer from the surface and the base is on the surface.

These rules give guidance regarding which surface modifications will improve alkane activation by oxide. They also reduce the number of calculations that need to be performed when analyzing a specific oxide catalyst for a specific alkane.

***(2) Possible predictors for a quick screening of catalytic activity: oxygen vacancy formation, the binding energy of the products, the activation energy for breaking the C-H bond.***

Numerous experiments have concluded that the rate-limiting step in alkane activation is the breaking of the carbon-hydrogen bond to make an adsorbed alkyl and an adsorbed hydrogen atom. This means that one can screen alkane activation catalysts by calculating the activation energy for alkane dissociation and this is what we do in most of our calculations. Given the extremely large number of oxides and modified oxides, it is valuable to have more efficient ways of screening (or pre-screening) alkane activation by oxide catalysts. One of these predictors is based on the Brønsted-Evans-Polanyi rules, which say that the stronger the alkane dissociation products (namely H and the alkyl) bind to the surface, the lower the activation energy to break the C-H bond. This allows us to efficiently compare the activity of various oxides by calculating binding energies instead of activation energies. Binding-energy calculations are more efficient, by a factor 20, than activation energy calculations. An even simpler procedure is to compare the ability of various oxides or modified oxides to function as oxidation catalysts by calculating how much energy it takes to remove oxygen from the surface (to make an oxygen vacancy). This is a reasonable descriptor because practically all catalytic chemistry of alkanes is partial oxidation and it has been shown that the oxygen in the product originates from the surface of the oxide, not from the oxygen present in the gas. That is, the oxide surface oxidizes and the gas phase oxygen replenishes the oxygen lost by the surface. In a recent paper[7], involving computations and experiments, we have shown that there is a linear relationship between the energy of oxygen-vacancy formation calculated by DFT and the activation energy for methane oxidation catalyzed by  $\text{La}_2\text{O}_3$  doped with a variety of cations.

***(3) Implications of the acid-base rules for alkane activation.*** Our Lewis acid-base rules suggest that because the dissociation fragments of an alkane are Lewis bases, the oxide should be modified to become a Lewis acid. This will make the dissociative-adsorption reaction more exoergic and lower the activation energy for breaking the C-H bond. We have shown that this can be achieved in two ways. (a) Doping the oxide with a lower valence dopant ( $\text{CaO}$  doped with Li,  $\text{ZrO}_2$  with La, etc.) creates a deficit of electrons in the surface and converts a surface oxygen into a Lewis acid. This increases substantially the binding energy of basic fragments (H and alkyl) to the surface. The Brønsted-Evans-Polanyi rules suggest that this change in the binding energy of the products will lower the activation energy for dissociative adsorption, which is true in all calculations we have performed so far[3,5,6; and our earlier work]. (b) Doping an oxide with a higher valence dopant (e.g.  $\text{CaO}$  doped with La) creates a Lewis-basic site on the surface because a trivalent atom (La) replaces a divalent one (Ca). According to our rules, oxygen (which is a Lewis acid) adsorbs on or near the higher-valence dopant, takes electrons from it, and becomes chemically active. This activated oxygen reacts readily with an

alkane and breaks the C-H bond. This is a new mechanism, proposed by us, which is the opposite of the Mars-van Krevelen mechanism; in our case the oxygen in the oxidation products originates from the gas, while in the MvK mechanism it originates from the surface of the oxide. Experiments with  $^{18}\text{O}_2$  that showed that this computational prediction is correct[27].

**(4) A general mechanism for alkane dissociative adsorption on oxide catalysts.** In any dissociative adsorption, the reaction breaks a bond and makes two (each dissociation fragment binds to the surface). In general, the activation energy is lower if the new bonds are formed while the old bond is broken. This is not possible for alkane dissociation on oxides because the distances between the binding sites are much larger than the C-H bond length. We found that this factor controls the reaction path for alkane dissociation. In all cases we have examined, regardless of the chemical nature of the oxide (doped or not) or of its morphology (being supported on a metal or another oxide, or being pure, or having a step), the dissociation took place by a disconcerted mechanism: first a hydrogen atom made a bond with a surface oxygen atom and then the alkyl tumbles on the surface to find a binding site. There are two transition states along this reaction path. During this motion the alkyl is weakly bonded to the surface and as a result, the rate for producing a hydroxyl and an alkoxide on the surface is comparable to that of producing a hydroxyl on the surface and an alkyl in the gas phase. These results suggest the possibility of parallel mechanisms: one produces an alkyl bonded to the surface and the other produces an alkyl in the gas. This possibility has been debated in the experimental literature and Lunsford has shown conclusively that gas phase radicals are produced during the oxidative coupling of methane on MgO. We suggest that this is likely to be general when the reaction is carried out at high temperature. There have been numerous suggestions by experimentalists that in high-temperature alkane catalytic activation, gas phase radical formation is important. Our calculations support this conclusion and also explain that the formation of a gas phase alkyl is caused essentially by the large distance between the binding sites for the dissociation fragments. Given the structure of oxides this is an unavoidable feature for all oxides.

**(5) A few specific discoveries regarding catalysis by oxides.** We have examined[2] the interaction of oxygen with a series of higher valence dopants in  $\text{La}_2\text{O}_3$  to answer the following general question: how does a dopant having a higher valence than the cation it substitutes affect the catalytic activity of the oxide? We found some unexpected behavior: the dopant donates an electron to the surface to make a polaron even though the host oxide is irreducible; the oxygen adsorbs at the polaron site and it is activated; there are very substantial differences between dopants from the left-hand side of the periodic table (e.g. Ti, Zr, Nb, Ta) and those in the right-hand side (e.g. Ge, Sn, As, Sb). This “overturned” the previous paradigm that the valence of the dopant is the major factor controlling its chemistry. Paper 3 studied the role of steps in methane dissociation on Na-doped with alkali. We found that the dopant prefers to be imbedded in the edge of the step and that the stepped surface is much more active for methane activation than the flat one. Paper 4 shows that during methane dissociation, the H and the  $\text{CH}_3$  radicals form a hydride and a methoxide even though when they bind alone they prefer to bind to oxygen. This is another example of the dramatic influence of the acid-base interaction we discovered in previous work. Paper 7 performed experiments to test a prediction made by our computations. We found that the measured activation energy for methane partial oxidation is a linear function of the calculated energy of oxygen vacancy formation. Papers 8-9 are experimental and had two purposes: to show that doped oxides are better methane partial oxidation catalysts than undoped

oxides (a thesis which our calculations developed); and that the catalyst under working conditions is the reduced doped oxide.

**(6) Effect of the halogenation of an oxide surface on its catalytic activity.** There have been many experiments that indicated that the presence of halogens on an oxide surface improves (in the vast majority of cases) its catalytic activity for alkane activation. We have examined such a system in the past work sponsored by AFOSR and continued these investigations under the current grant. In paper 11 we showed that the presence of an adsorbed halogen on an oxide surface makes it easier to make oxygen vacancies and therefore makes the oxide a better oxidant. This fact is in agreement with our acid-base rules: the halogen is an acid and making an oxygen vacancy creates a base; hence a strong acid-base interaction facilitates the formation of the vacancy. Then we thought (along with a number of experimentalists) that an oxychloride might be a good model for explaining the role of halogenation. We found that we were wrong: the oxychloride is a very inert compound and worthless catalyst. We remained, however, very curious about the possible effect of halogens and decided to examine their role in gas phase alkane reactions. We found[11,13] that addition of  $I_2$  catalyzes the hydrogenation of  $CH_2Br_2$  and the formation of propylene from propane. We proposed that  $I_2$  is a gas phase catalyst and we currently believe that this system will lead to a higher propylene yield than the current industrial processes.

**(7) Oxide clusters supported on metals or on oxides.** A possible modification of an oxide is to create submonolayers supported on a metal or on an oxide. We have shown that isolated  $VO_4$  clusters supported on Au or Ag are good methane activation catalysts[14]. That paper also made an intriguing observation, that many high-energy isomers of the cluster are as good catalysts as the low-energy ones: the energy required to create the isomer is compensated by the fact that the isomer has lower activation energy for methane dissociation; the populations of these isomers are low but they react much faster. For paper 20 we prepared in ultra-high vacuum mass-selected vanadium oxide clusters supported on  $TiO_2$  and studied their catalytic activity for methanol oxidation to formaldehyde. This is part of our effort to study well-defined catalysts to understand the connection between activity and clusters size and composition.

**(8) Are sulfides similar to oxides?** During the reporting period we became interested in a project whose aim was to develop a HBr flow electrochemical cell for energy storage using a sulfide electrode. We got involved in this project partly because we assumed that sulfides are similar to oxides and therefore we had an opportunity to test whether the acid-base rules we proposed for oxides, work also for sulfides. The result is that they do not. Nevertheless we published a number of interesting experimental-computational work[15-19] which tested a variety of sulfide electrodes and performed experiments (and calculations) to find out why sulfides performed poorly for the electrochemical hydrogen oxidation.

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## APPENDIX

### *Computational Study of a Model Inverse Catalyst and of Defects in an Oxide Surface*

Jie Yu

Ph.D. dissertation, University of California, Santa Barbara, 2013

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### Summary

In recent years, significant research efforts on fundamental catalytic research have been undertaken, driven by the need to control and improve heterogeneous catalysis processes at a molecular level. Model systems have been designed and studied to investigate catalytic processes, while most of the work so far has involved metal nanoparticles deposited on oxide supports. Recently, another type of model catalyst system has been suggested which consists of a metal single-crystal surface decorated with submonolayer quantities of an oxide phase. This “inverse-catalyst model system” offers interesting possibilities to explore the effects of the metal-oxide interface on the reactivity.

We use density functional theory, with the GGA-PBE functional, to investigate the ability of vanadium oxide clusters, supported on Ag or Au, to break the C-H bond in methane. We perform a thermodynamic analysis to show that the VO<sub>4</sub> cluster is the most likely oxidant and then proceed to calculate the energy of the dissociative adsorption of methane and its activation energy with the Nudged Elastic Band (NEB) method. It appears that isolated VO<sub>4</sub> clusters supported on Au (111) are promising catalysts for the first step in methane activation, the breaking of the C-H bond. We explain some peculiar features of the reaction path and propose that they are general for alkane activation on oxides.

We also observe that the support makes a substantial difference and that Au is a much better support than Ag. This probably happens because Au makes weaker bonds with the oxygen in VO<sub>4</sub>, or, equivalently, because VO<sub>4</sub> binds less strongly to Au than to Ag. We propose that if one compares the activity of the same cluster on a variety of supports, then the reaction energy for the dissociative adsorption is higher when the bond of the cluster to the support is weaker. We emphasize that these “rules” are, at this point, based on very few examples and need to be tested further.

An important role in catalysis is the surface mobility of active species in the catalytic process and also during activation or regeneration treatments of the catalysts. To quantify the degree of difficulty for VO<sub>4</sub> clusters to move on Au (111) and Ag (111) surfaces, we calculate, by using the NEB method, the energy barrier for the motion of the VO<sub>4</sub> cluster along the surface. The energy barrier for VO<sub>4</sub> moving on a silver surface is higher than that on a gold surface, which is not surprising considering the bonding character between the cluster and metal surfaces. The high mobility verifies our observation that the bonding connection between the cluster and the surface is much weaker after the dissociation and less sensitive on the positions of the VO<sub>4</sub> cluster. We observe that the adsorption and the dissociation of methane on the cluster are equally probable for all intermediate cluster geometries during the motion from one lattice site to another.

As another model system for catalysis, MgO oxide surfaces have been an active research topic in the last decade and it is believed that oxygen vacancies on oxide surfaces can participate in various chemical reactions. The formation of oxygen vacancies on MgO surfaces has been

studied extensively. However, previous work has mainly been limited to the neutral case and the studies of charged defects mainly focus on their geometric and thermodynamic properties. Furthermore, the doping effect is barely included in the previous theoretical works due to its complexity. Here, we study the geometric and electronic properties of the oxygen vacancies with different charge states on the MgO (001) surface. We have developed a methodology for calculating charged defect formation energies at surfaces. From first-principles calculations we obtain the formation energies of the oxygen vacancies on MgO surface with 0, +1, +2, and -1 charge states under both oxygen-rich and oxygen-poor conditions. We investigate the effects of doping on the formation energy and concentration of oxygen vacancies. The doping effect is considered in our calculations through the corresponding change of the Fermi level. We further study the absorption of oxygen molecules at these vacancies, calculate their relative energetic stability, and analyze its implication on their surface catalytic properties. This study sheds light on the catalytic activity of charged oxygen vacancies on oxide surfaces.

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## Abstract

The overall goal of this work has been to find chemical and modifications of oxide surfaces that boost their catalytic performance for alkane conversion. Experimental work is done in collaboration with UCSB Professors Michael J. Gordon and Eric W. McFarland. We have examined a large number of modifications: doping with higher-valence or lower-valence cations, halogenating the surface, delaminating some oxides to turn them in two-dimensional materials, creating submonolayers of oxides supported on other oxides or on metals, or promoting oxide catalytic chemistry by using molten salts. Based on calculations on a variety of oxide-molecule systems, we proposed a set of general rules that give guidance regarding which surface modifications will improve alkane activation by an oxide catalyst and reduce the number of calculations that need to be performed when analyzing a specific oxide catalyst for a specific alkane. For example, the presence of an acid on a surface will change the site to which a base will bind and will increase substantially the binding energy of the base. This

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strong acid-base interaction takes place through the oxide; the base does not bind to the acid. The acid will influence the binding of the base even if the binding site is several lattice sites away. The same phenomena occur if an acid binds to a surface on which a base is present. Prior to this work it was assumed that in the presence of another species, a molecule will bind to the site to which it binds when it is alone on the surface; this is not true if one molecule is an acid and the other is a base. These rules have been used to guide us in deciding which modifications of an oxide surface will increase the catalytic activity for alkane activation. Essentially we found that all lower-valence dopants will activate surface oxygen, making the Mars-van Krevelen mechanism for alkane partial oxidation more efficient. Higher-valence dopants will adsorb O<sub>2</sub>, transfer electrons to it, and make it more reactive. Our calculations and experiments have shown that this activated oxygen will react more readily with alkanes than it would on an undoped oxide. We have also studied how the reactivity of oxide clusters supported on a metal (Au or Ag) or on an oxide is modified by the interaction with the support and the fact that they have a small number of atoms. This research is also a combination of computations and experiments. In the course of this studies we proposed a number of predictors that allow a quick screening of various oxide catalysts (modified or not): the energy of oxygen vacancy formation, the binding energy of the products, the activation energy for breaking the C H bond. We performed experiments that confirm that the activation energy for methane partial oxidation catalyzed by La<sub>2</sub>O<sub>3</sub> doped with a variety of cations is a linear function of the energy of oxygen-vacancy formation calculated by DFT. This validated the suggestion that the energy of vacancy formation is a good predictor for the activity of a alkane conversion catalyst. Finally, by examining many examples we have found that the reaction of dissociative adsorption of an alkene on an oxide (modified or not, with or without steps, or supported on a metal) has the same disconcerted mechanism: the hydrogen binds to an oxygen atom of the surface and then the alkyl performs a large displacement on the surface to find a binding site. In all cases the activation energy to remove the alkyl from the surface is comparable to that of the reaction in which the alkyl binds to the surface. We propose that all high-temperature catalytic alkane activation reactions on oxide produce gas phase radicals. There is experimental confirmation for this suggestion.

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Catalysis by doped oxides, Eric W. McFarland and Horia Metiu, Chemical Reviews 113, 4391-4427 (2013). DOI: 10.1021/cr300418s

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**Program Officer**

**Research Objectives**

**Technical Summary**

**Funding Summary by Cost Category (by FY, \$K)**

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Equipment/Facilities			
Supplies			
Total			

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